Effect of ions on sulfuric acid-water binary particle formation : 2. Experimental data and comparison with QC-normalized classical nucleation theory

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Key Points:
- Atmospheric binary particle formation can be both kinetic and nucleation type
- Both ion-induced and neutral pathways are strong at free-tropospheric conditions
- Ion-induced pathway dominates at midtroposphere, neutral at upper troposphere

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Effect of ions on sulfuric acid-water binary particle formation: 2. Experimental data and comparison with QC-normalized classical nucleation theory

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Abstract We report comprehensive, demonstrably contaminant-free measurements of binary particle formation rates by sulfuric acid and water for neutral and ion-induced pathways conducted in the European Organization for Nuclear Research Cosmics Leaving Outdoor Droplets chamber. The recently developed Atmospheric Pressure interface-time of flight-mass spectrometer was used to detect contaminants in charged clusters and to identify runs free of any contaminants. Four parameters were varied to cover ambient conditions: sulfuric acid concentration (10^5 to 10^9 mol cm^{-3}), relative humidity (11% to 58%), temperature (207 K to 299 K), and total ion concentration (0 to 6800 ions cm^{-3}). Formation rates were directly measured with novel instruments at sizes close to the critical cluster size (mobility size of 1.3 nm to 3.2 nm). We compare our results with predictions from Classical Nucleation Theory normalized by Quantum Chemical calculation (QC-normalized CNT), which is described in a companion paper. The formation rates predicted by the QC-normalized CNT were extended from critical cluster sizes to measured sizes using the UHMA2 sectional particle microphysics model. Our results show, for the first time, good agreement between predicted and measured particle formation rates for the binary (neutral and ion-induced) sulfuric acid-water system. Formation rates increase with RH, sulfuric acid, and ion concentrations and decrease with temperature at fixed RH and sulfuric acid concentration. Under atmospheric conditions, neutral particle formation dominates at low temperatures, while ion-induced particle formation dominates at higher temperatures. The good agreement between the theory and our comprehensive data set gives confidence in using the QC-normalized CNT as a powerful tool to study neutral and ion-induced binary particle formation in atmospheric modeling.

1. Introduction

The majority of aerosol particles in Earth's atmosphere are estimated to originate from gas-to-particle transformation [*Merikanto et al.*, 2009]. Sulfuric acid has long been thought to be one of the main species initiating particle formation in the atmosphere due to its low vapor pressure and its strong affinity for water. Recent findings show that trace levels (a few parts per trillion (ppt)) of other species, e.g., amines [*Murphy et al.*, 2007;

Kurten et al., 2008; *Kürten et al*., 2014; *Almeida et al*., 2013; *Bianchi et al*., 2014], oxidized organics [*Kulmala et al*., 2004; *Zhang et al*., 2009; *Metzger et al*., 2010; *Riccobono et al*., 2012; *Schobesberger et al*., 2013; *Ehn et al*., 2014; *Riccobono et al*., 2014], and ammonia [*Ziereis and Arnold*, 1986; *Ball et al*., 1999; *Kirkby et al*., 2011; *Schobesberger et al*., 2015] likely contribute to particle formation in the lower troposphere [*Kulmala et al*., 1998; *Zhang et al*., 2012; *Kulmala et al*., 2013; *Berndt et al*., 2014]. Observations in the atmospheric boundary layer suggest that new particle formation takes place mainly through a neutral pathway, with an ion-induced contribution of only around 10% [*Laakso et al*., 2007; *Manninen et al*., 2009].

In the upper troposphere and lower stratosphere, where the temperature is low, binary water-sulfuric acid nucleation processes may be important sources of new particles. At these altitudes, particle formation can also be significantly enhanced by species such as ammonia [*Ball et al*., 1999; *Kirkby et al*., 2011]. The binary formation of new particles that are initially around 1 nm in diameter can also be significantly enhanced by the presence of ions [*Raes and Janssens*, 1986; *Lovejoy et al*., 2004; *Kirkby et al*., 2011] that mainly derive from cosmic rays. These nanometer-sized particles can subsequently grow to 50–100 nm, sufficiently large to act as cloud condensation nuclei (CCN). Therefore, changes in atmospheric particle formation by ions could potentially affect CCN concentrations and cloud properties.

The impact of solar variation on climate has been widely discussed [e.g., *Kirkby*, 2007; *Gray et al*., 2010]. Solar activity variation modulates the cosmic ray flux entering the atmosphere and could potentially modulate cloud properties through an ion-particle formation-particle growth-CCN link. The CLOUD (Cosmics Leaving OUtdoor Droplets) project at European Organization for Nuclear Research (CERN) investigates the effects of galactic cosmic rays on aerosol and cloud formation, and hence on climate. Here we report neutral and ion-enhanced water-sulfuric acid particle formation rates (referred hereafter to as the binary process) measured during the CLOUD5 campaign in 2011; we compare the measurements with the QC-normalized Classical Nucleation Theory (CNT) [*Merikanto et al*., 2016]. In a companion paper [*Merikanto et al*., 2016] (hereafter referred to as Paper 1), we give a full representation of this most recent version of CNT. The measurements were carried out at temperatures, sulfuric acid concentrations, relative humidities, and ion concentrations spanning tropospheric conditions. Throughout both papers, we use the term "particle formation" generally to describe the generation of new particles from the vapor phase and use the term "nucleation," which is often used synonymously, only when this process involves the crossing of a free-energy barrier, at the top of which is located at the critical cluster size.

Besides its atmospheric significance, knowledge of the binary process is vital for understanding processes involving more than two components and atmospheric particle formation as a whole. Despite extensive research over many decades, measurements of particle formation lack the precision and coverage of relevant tropospheric conditions to enable quantitative model evaluation; moreover, they suffer from inadequate control over impurities. As a result, theoretical models describing the process have yet to be fully validated. During CLOUD5, we were able to measure the particle formation rate at very small particle sizes while simultaneously monitoring the cluster composition. The CLOUD chamber experiments use the state-of-art instruments while ensuring ultraclean conditions [*Kirkby et al*., 2011; *Bianchi et al*., 2012; *Praplan et al*., 2012; *Schnitzhofer et al*., 2014; *Almeida et al*., 2013]. This unique facility, combined with the broader CERN facilities and expertise, has made it possible to run experiments with extremely low levels of impurities, while spanning the extreme temperatures encountered in different regions of the atmosphere, thereby providing data that fill this critical gap in our understanding.

1.1. Brief Review of Water-Sulfuric Acid Particle Formation Experiments

The search for an accurate understanding of binary water-sulfuric acid particle formation has a long history, which is briefly reviewed here. The first quantitative laboratory experiments were made by *Reiss et al*. [1976] in a piston cloud chamber; these studies were followed by reactor experiments conducted by *Boulaud et al*. [1977] and experiments in an upward thermal diffusion cloud chamber by *Mirabel and Clavelin* [1978]. *Cox* [1973] and *Friend et al*. [1980] conducted flow reactor studies of gas-to-particle conversion involving sulfuric acid produced during photooxidation of sulfur dioxide (SO_2). These studies demonstrated the likely atmospheric significance of sulfuric acid-water particle formation originally suggested by binary CNT [e.g., *Reiss*, 1950; *Mirabel and Katz*, 1974; *Shugard et al*., 1974], but the thermodynamic data and instrumentation available in that era limited the rigor with which experimental and theoretical results could be compared.

Nonetheless, the experimental results stimulated advances in the theoretical work. CNT was updated to include the effects of hydrate formation due to the strong binding affinity of sulfuric acid to water [e.g., *Heist and Reiss*, 1974; *Shugard and Reiss*, 1976; *Jaecker-Voirol and Mirabel*, 1988; *Lazaridis et al*., 1991; *Kulmala et al*., 1991]. Accurate quantitative theoretical prediction of nucleation rates requires thermodynamic data on properties like surface tension and equilibrium vapor pressure over the temperature and pressure range of the experiments, but the available data were highly uncertain. For example, in the late 1970s the suggested values of equilibrium vapor pressure for pure sulfuric acid ranged from about 1.3×10^{-9} atm to 5×10^{-7} atm at 298 K [*Gmitro and Vermeulen*, 1964; *Doyle*, 1961; *Kiang and Stauffer*, 1973], thus introducing a large uncertainty into theoretical predictions. The first measurements of the equilibrium vapor pressure of sulfuric acid were conducted by *Roedel* [1979], who found a value of 3.29×10^{-9} atm at 296 K. Later measurement results by *Ayers et al*. [1980] were close to those of *Roedel* [1979] (lower by a factor of 3), even though the latter measurements were performed at much higher temperatures (338–445 K). Measurements of the equilibrium vapor pressure of sulfuric acid at 300–343 K by *Marti et al*. [1997] generally agree with the predictions of *Ayers et al*. [1980], although the observed vapor pressure exceeded that predicted for the more dilute solutions. The experimental equilibrium vapor pressure expression of *Ayers et al*. [1980], later extrapolated to atmospheric temperatures by *Kulmala and Laaksonen* [1990], is used today in binary nucleation calculations [e.g., *Vehkamaki et al*., 2002]. We shall also employ that expression in this study.

Wyslouzil et al. [1991] published the first temperature-dependent nucleation rate data (nucleation temperatures, $T_{nuc}=293.3$, 298.3, and 303.3 K) for the sulfuric acid-water system. Their measurements differed from the theoretical Jaecker-Voirol-Mirabel nucleation rates by a factor varying between 10^{-11} and 10^{12}. On the other hand, in flow-tube experiments using Titrisol® solutions of sulfuric acid in water, *Viisanen et al*. [1997] obtained agreement between the measured rates and the hydrate-corrected and thermodynamically consistent version of CNT by *Wilemski* [1987]. The sulfuric acid concentration was not directly measured in either of these studies; instead, it was calculated from mass balance considerations or from the saturation vapor pressure or molality of a weak sulfuric acid solution.

Using a selected ion chemical ionization mass spectrometer [*Eisele and Tanner*, 1993], *Ball et al*. [1999] performed the first experiments (at 295 K) in which the sulfuric acid vapor concentration was directly measured. They also detected freshly nucleated particles down to 3 nm (>50% detection efficiency) with an Ultrafine Condensation Nucleus Counter [*Stolzenburg and McMurry*, 1991], thereby providing the most comprehensive data set on sulfuric acid-water nucleation at that time. Both the measurements of *Ball et al*. [1999] and those of *Viisanen et al*. [1997] are in reasonable agreement with predictions made using the rigorous theoretical approach of *Noppel et al*. [2002] (see Paper 1). Hence, this theoretical approach was used in the widely applied nucleation parameterization by *Vehkamaki et al*. [2002]. Binary nucleation data for the sulfuric acid-water system can be found also in the work of *Zhang et al*. [2004], who also used an ultrafine condensation particle counter and a mass spectrometer to detect and characterize forming particles, although their work was primarily focused on the enhancement of nucleation by organic acids. Both *Ball et al*. [1999] and *Zhang et al*. [2004] used pure liquid sulfuric acid as a source of sulfuric acid vapor; the results of these two studies agree closely.

During the last decade, most experimental studies of the neutral binary system focused on particle formation under atmospheric boundary layer conditions, and, except for the CLOUD continuously stirred tank reactor (CSTR) experiments, relied on flow-tube techniques. These experiments have produced gas phase sulfuric acid by a photooxidation of SO_2 [e.g., *Berndt et al*., 2005; *Benson et al*., 2008; *Young et al*., 2008; *Sipila et al*., 2010, *Kirkby et al*., 2011] or by evaporation from dilute solutions [*Brus et al*., 2010, 2011] or neat sulfuric acid [*Zollner et al*., 2012]. Binary homogeneous nucleation results from these studies were often in stark disagreement with the parameterization of *Vehkamaki et al*. [2002], but the source of sulfuric acid vapor also appeared to affect the experimental outcomes. Two experimental limitations apply to these experiments: contamination by minute but significant levels of trace gases, and a significant difference between the extremely small critical cluster size and the minimum measurable particle size. Until very recently, no measurement techniques existed to address either limitation.

Even though these recent studies were executed with care and purported to address binary nucleation, most were, to some extent, burdened with *ppt* level contamination by base impurities like ammonia and amines.

These trace-level contaminants were shown to arise from various sources such as the water used for carrier gas humidification, the carrier gas itself, or simply surfaces in the experimental system [e.g., *Benson et al*., 2011; *Brus et al*., 2011; *Kirkby et al*., 2011]. Only recently have advances in analytical techniques like mass spectrometry [e.g., *Ehn et al*., 2010; *Junninen et al*., 2010; *Zhao et al*., 2010; *Jokinen et al*., 2012; *Schobesberger et al*., 2015] and ion chromatography [*Praplan et al*., 2012] made it possible to monitor these low-level impurities in the formed molecular clusters and in the gas phase. The first experiments at CLOUD [*Duplissy et al*., 2010; *Kirkby et al*., 2011] were designed to address binary nucleation alone, but only after new measurement methods were employed, trace contamination by ammonia was detected and subsequently reduced.

Newly developed detectors have also pushed size cutoffs close to the critical cluster size [*Iida et al*., 2009]. These include the Particle Size Magnifier (PSM) [*Vanhanen et al*., 2011], diethylene-glycol condensation particle counters (DEG-CPC) [*Wimmer et al*., 2013], and the pulse height analyzer ultrafine condensation particle counter (PHA-UCPC) [*O'Dowd et al*., 2004]. These detectors have achieved sufficient sensitivity to directly count particles below 3 nm in diameter, contributing to uncovering the reason behind the discrepancies among the sulfuric acid power dependencies of formation rates in the previous studies, even though the contamination problems remained [*Sipila et al*., 2010].

Discrepancies between different measurements have been shown to arise from contamination and depletion of sulfuric acid in the flow tube, hampering the growth of formed particles to observable sizes before being lost to the walls, together with the fact that different instruments have different cutoff sizes, and transmission curves that are also not step functions at the cutoff diameter. Reviews and discussion of the results of experimental studies performed to date can be found in the existing literature [e.g., *Brus et al*., 2010; *Zollner et al*., 2012; and *Zhang et al*., 2012]. *Ehrhart and Curtius* [2013] have shown that for experimental conditions, where growth rates are slow compared to the loss rates of clusters to either the reactor walls or larger aerosol particles, derived nucleation rates, and their dependencies on the H_2SO_4 concentration are influenced by the loss processes. This finding suggests another reason for diverging experimental results as the loss processes differ from experiment to experiment.

1.2. Brief Review of the Effect of Ions on Particle Formation Studies

The impact of ionizing radiation on particle formation was first studied in the late nineteenth century by Wilson, who irradiated an expansion chamber with X-rays and radioactive materials, e.g., uranium, and observed that the ions induced droplet formation [*Wilson*, 1895, 1899]. Later experiments [*Metnieks and Pollak*, 1959; *Megaw and Wiffen*, 1961] explored the link between the strength of radiation and the concentrations of the resulting particles. *Vohra et al*. [1984] observed enhanced particulate sulfate production when radon was injected into a mixture of SO_2, O_2, and C_2H_4. The effect of UV and gamma rays on particle formation in a gaseous mixture of SO_2 and NO_2 was investigated by *Raes et al*. [1985]. *Mäkelä et al*. [1995] performed experiments in which humid air containing SO_2 was irradiated and showed that the bimodal size distribution predicted by the ion-induced CNT was qualitatively correct. *Kim et al*. [1997] quantitatively compared ion-induced and neutral binary nucleation at various levels of SO_2 as well as water vapor and various irradiation times by α-rays and concluded that the contribution of ion-induced to total nucleation was lowered when the concentration of SO_2 was increased.

Lovejoy et al. [2004] measured the thermodynamics of small cluster ions containing sulfuric acid and concluded that, while ion-induced particle formation cannot explain observations in the boundary layer, the process can be significant in the middle and upper troposphere. In a study of particle nucleation at atmospherically relevant concentrations of SO_2, O_3, and water vapor, *Svensmark et al*. [2007] reported that the production of particles under these conditions is proportional to the negative ion density and hypothesized that atmospheric ions continuously generate a reservoir of ready-to-grow thermodynamically stable clusters. In a pilot CLOUD chamber experiment, *Duplissy et al*. [2010] investigated the effect of ionizing particle radiation on aerosol formation from trace H_2SO_4 vapor ($\leq 10^6$ mol cm^{-3}). They concluded that ion-induced nucleation or ion-ion recombination was a source of particles. In later CLOUD1-CLOUD3 measurements, *Kirkby et al*. [2011] reported a clear enhancement in binary particle formation rates due to ions at 248 K. The CLOUD5 data presented here are verifiably from the binary H_2SO_4/H_2O system and cover a wide range of tropospheric conditions. We also show that Classical Nucleation Theory normalized by Quantum Chemical calculation (QC-normalized CNT), described in Paper 1, can describe the process with remarkable accuracy.

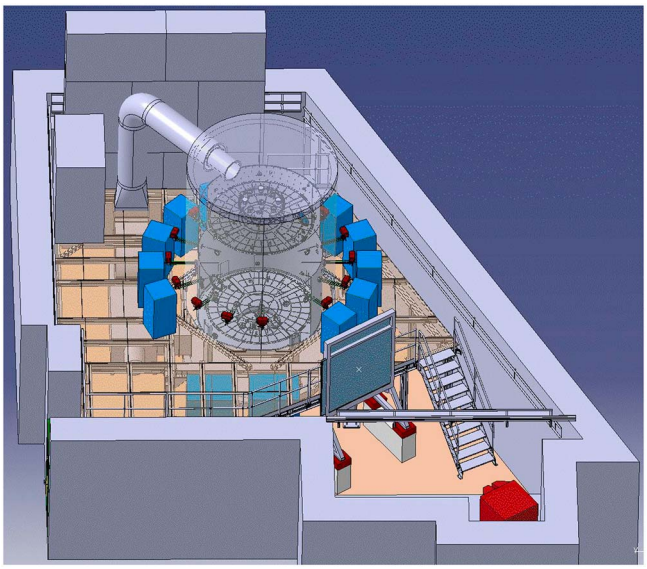

Figure 1. An illustration of CLOUD in the T11 experimental zone at the CERN PS. The defocused particle beam exits a dipole magnet (bottom right), crosses the aluminum hodoscope counter (middle), and then traverses the 3 m diameter CLOUD chamber before being stopped by the concrete wall (top left). The instruments (blue boxes) analyze the contents of the chamber via sampling probes. Air at a precisely controlled temperature circulates between the chamber and the thermal housing. Both the thermal housing and the chamber are shown partly transparent, revealing the circular field cage electrodes that create the clearing field for the removal of ions (bottom and top part of the chamber).

2. Methods

2.1. CLOUD Chamber

Here we describe the CLOUD chamber, focusing on the setup during the CLOUD5 experiment. A short general description of the CLOUD chamber can be found in the supporting information of *Kirkby et al.* [2011]. The CLOUD chamber is installed on the T11 beam line in the East Hall at the CERN Proton Synchrotron (PS) (Figure 1). Because the CLOUD chamber is not underground, it is continuously exposed to galactic cosmic rays (GCR). In addition to galactic cosmic rays, the chamber can be exposed to a 3.5 GeV/c secondary pion beam (π beam) from the CERN PS. This beam corresponds to the characteristic energies and ionization rates of cosmic ray muons in the lower troposphere. The CERN PS π beam is typically highly focused, but for the CLOUD experiment it is defocused to a transverse size of about $150 \times 150\,cm^2$ across the chamber. The beam intensity can be adjusted to span the natural range of equilibrium ion-pair (i.p.) concentrations from ground level (about 200 i.p. cm^{-3}) up to stratospheric values (about 6000 i.p. cm^{-3}) [*Duplissy et al.*, 2010]. Any intermediate setting between these minimum and maximum levels can be achieved by adjusting the beam collimators or the frequency of the π-beam cycle. Even though galactic cosmic rays are always present, the ion-pair concentration can also be reduced down to a few i.p. cm^{-3} by applying a high-voltage clearing electric field inside the chamber. To achieve this, a high-voltage field cage comprising two electrodes is installed inside the chamber. Voltages in a range of ± 30 kV can be applied to the two electrodes. When high voltage is applied, these electrodes create an internal electric field of up to 20 kV m^{-1}, thus removing all ions within a second (which is much shorter than the typical interval between collisions of relevant molecules, ~1000 s for a sulfuric acid concentration of 10^7 cm^{-3}).

A technical schematic of the CLOUD chamber is shown in Figure 2. The chamber is a 3 m diameter ~3.5 m high electropolished, 316 L stainless steel cylinder (26.1 m^3). Grounded stainless steel enables much better control over the concentration of ions than is possible with a traditional Teflon chamber, where most ions would be stripped away and charges accumulating on the Teflon surfaces produce uncontrollable electric fields. The stainless steel also allows a higher standard of cleanliness. Two stainless steel fans are mounted inside the chamber at the bottom and the top; these are magnetically coupled to flexible drives connected to motors located outside the chamber. The fans run in counter flow to achieve efficient turbulent mixing of the gases and the ions in the chamber [*Voigtlaeander et al.*, 2012].

The chamber is surrounded by an insulated thermal housing and has been designed to achieve a high standard of temperature stability. The CLOUD chamber temperature is controlled by precisely regulating the temperature of air circulating in the space between the chamber and the thermal housing (see Figures 1 and 2). Experimental runs can presently be performed at temperatures between 207 K and 310 K, and they are stable to within 0.1 K. During chamber cleaning, the temperature can be raised to 373 K. Forty temperature sensors monitor the temperature of the chamber's external wall. A string of 5 PT100 temperature sensors is placed at midplane level inside the chamber, at distances of 0.05, 0.2, 0.4, 0.8, and 1.2 m from the chamber wall. The value at 1.2 m distance is used as the chamber's reference temperature and is symbolized with a "T" in Figure 2.

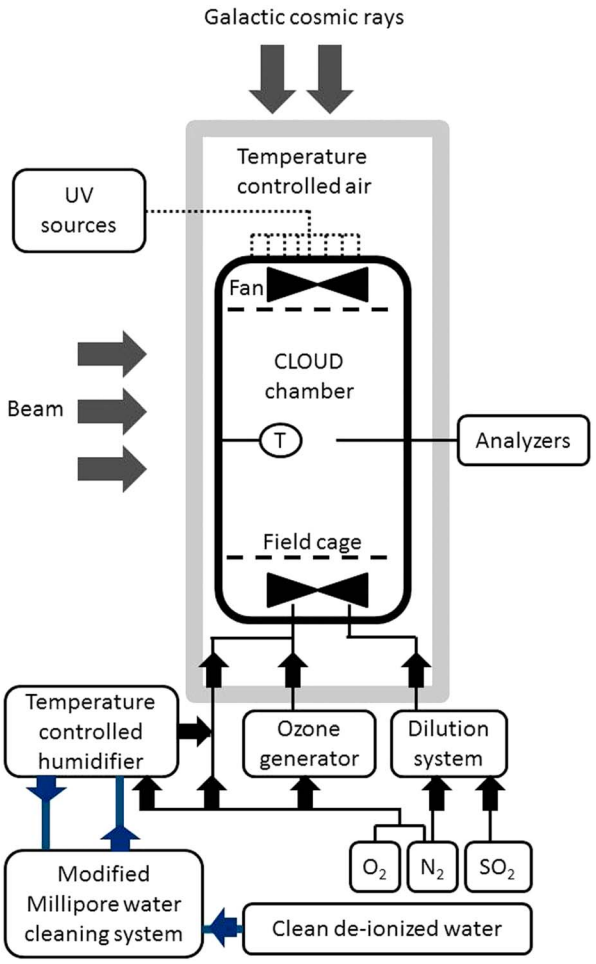

Figure 2. CLOUD experiment schematic. Clean deionized water is introduced to a modified Millipore water cleaning system where it is recirculated and filtered continuously. Water vapor is added to purified dry air via a Nafion membrane in the humidifier. All different gases (SO_2, O_3, and humid air) have their own line and arrive at the bottom of the chamber, just below a mixing fan. Inside the chamber, two fans, one at the bottom and one at the top, work in counter flow to ensure uniform mixing of the gases. The inside of the chamber can be irradiated by UV light introduced from the top of the chamber. Ions are produced by galactic cosmic rays and additionally by using the CERN PS beam. A clearing field can be switched on to remove the ions when needed. The chamber is surrounded by a thermal housing. Temperature-controlled air is circulated around the chamber to maintain a constant temperature inside the chamber.

CLOUD is filled with ultrapure synthetic, humidified air. Ultrapure dry air is obtained from the evaporation of cryogenic liquid N_2 (Carbagas, 99.9999%) and liquid O_2 (Carbagas 99.998%), which are mixed in a 79:21 ratio. A portion of the flow passes through a Nafion humidifier and is then mixed with the ultrapure dry air. Deionized water is continuously recirculated in an adapted Millipore Super-Q system, which includes one active carbon cartridge (Millipore CDFC02203), two ion-exchange cartridges (Millipore CPMB02202), one active organic cartridge (Millipore CPEX02201), one 0.22 μm particle filter (Millipore CVDI01TPE), and ultraviolet radiation. The recirculated clean water is passed through a temperature-controlled Nafion humidifier (Perma Pure, FC150-480-10SSK). By precisely adjusting the temperature and air flow through the Nafion humidifier, the relative humidity in the CLOUD chamber can be adjusted and controlled. Great care has been taken to avoid any water condensation prior to the introduction of humid air into the chamber by heating the tube in which the gases are mixed. The humid air is then cooled down to the chamber's internal temperature prior to entering the chamber.

Trace gases are also controlled with care. Ozone is created in a separate glass flow tube by UV photolysis of the cryogenic O_2 using a UV lamp (SterilAir, 30W). The ozone concentration is regulated by adjusting the flow of oxygen being irradiated. It is then mixed with the main flow of air upstream of the point where that flow enters the chamber (Figure 2). Trace amounts of SO_2 are added from gas cylinders (Carbagas, 99.95%) with pressurized N_2 as the carrier. The input concentration of SO_2 is precisely regulated by the use of three mass flow controllers (MFC) and valves. The chamber and gas supply were designed to achieve and sustain the highest standards of cleanliness. All MFC, tubes, and connections are pure stainless steel without any organic components.

The contents of the chamber can be irradiated with UV light of adjustable intensity (0 to 124 mW m^{-2}) with wavelengths in the range 250–750 nm. The UV is produced by four Hamamatsu LC8 UV light sources (200 W Hg-Xe lamp) and is introduced via 239 optical fiber vacuum feedthroughs installed on top of the chamber [*Kupc et al.*, 2011]. Because the lamps and all electronics are outside the chamber, this system produces negligible heat load. The adjustable UV irradiation stimulates further reactions; in the case of CLOUD5, the oxidation of SO_2 to H_2SO_4 is triggered by the production of OH radicals, formed after photolysis of O_3 in the presence of H_2O. By varying the light intensity, the H_2SO_4 production rate can be adjusted.

Instruments can sample chamber air from 14 electropolished stainless steel sampling probes placed around the chamber, in the midplane level (where the clearing field is at 0 V). The probes are 0.75 m long and project 0.3 m into the chamber. Probe internal diameters of 10.4 or 22.35 mm are used, depending on the flow rate of sampling air, to avoid turbulence and to minimize losses. Actively cooled copper linings maintained at the chamber temperature have been brazed around the portions of probes extending out of the chamber to keep the temperature of the sampled air close to the chamber temperature. The contents of the chamber are continuously analyzed by instruments connected to the sampling probes. The total gas flow (including N_2, O_2, H_2O, O_3, and SO_2,) entering the chamber is kept constant at 140 L min^{-1}. The total inflow to the chamber is larger than the outflow to the instruments. An adjustable exhaust flow is used to maintain the chamber pressure a few hPa above ambient pressure. The high volume of the chamber allows experiments to last for several hours with a flushing time scale of 3 h in the case of CLOUD5 experiments. The mixing time scale of the chamber is short compared to the flushing time scale, and both input and output flows are kept constant, and thus the chamber operates as a CSTR. Well-defined start times ($t = 0$) for experiments are established by turning on UV illumination or by turning off (or on) the ion clearing field, or by opening the π beam.

Prior to the start of the campaign, the chamber was actively cleaned in three steps. First, high-pressure ultrapure water was used to rinse the inside wall of the chamber; second, the temperature was increased to 373 K while the chamber was flushed with wet ultrapure air for several days; and third, the chamber was continuously flushed with high concentrations of ozone (ppm level) for 1 day.

2.2. Analyzers

The CLOUD experiment is equipped with state-of-the-art ion, particle and trace gas detectors for a thorough investigation of the first steps of particle formation and growth. The instruments used during CLOUD5 and their application in this study are briefly presented below.

2.2.1. Galactic Cosmic Ray Flux and π-Beam Monitors

Galactic cosmic ray (GCR) fluxes are monitored by a GCR detector situated nearby but outside of the beam area. The GCR instrument consists of 120 gas-discharge cylindrical Geiger counters arranged in 12 blocks, each of which contains 10 counters. All blocks are located on a platform ~1 × 1 m in size. It provides, with 500 ms integration time, a continuous detection of total charged particle abundance that consists of galactic cosmic rays (secondary component), natural radioactivity, and any scattered particles produced by the particle PS beam. The π-beam intensity is measured by two independent scintillation counters. A plastic scintillation counter of 140 × 20 cm is placed immediately at the exit of the beam. A plastic scintillation counter hodoscope of overall size 180 × 180 cm, comprising nine vertical counters followed by nine horizontal counters all of the size of 180 × 20 cm, provides the vertical and horizontal beam intensity profile with a time resolution that can be adjusted from 25 ms up to few seconds [*Mizin et al*., 2011]. It is located 5.4 m from the beam exit in front of the CLOUD chamber (see Figure 1). The beam intensity measurements from the two scintillation detectors agree well with each other. A comparison of the data from the two scintillation counters and the ion production rate as a function of beam intensity, temperature, and humidity is presented in *Franchin et al*. [2015].

2.2.2. Ion Composition and Size Distribution Detectors

The concentration and size distribution of ions in the chamber that have electric mobility diameters ranging from 0.8 nm to 42 nm were measured with one Neutral cluster and two Air Ion Spectrometers (NAIS), one for positive ions and one for negative ions. The NAIS is a differential mobility analyzer in which sampled ions are collected simultaneously on 21 electrometer rings to produce parallel measurements of 21 electrical mobility fractions for each polarity (see *Manninen et al*. [2010] for details). An Atmospheric Pressure interface-Time Of Flight-Mass Spectrometer (APi-TOF-MS) measured the ion cluster mass spectra in the chamber. The instrument consists of a sampling inlet, Atmospheric Pressure interface (APi), and a high-resolution time-of-flight mass spectrometer. Chemical species are identified from their exact mass signatures and isotopic fractions, for positive and negative ions up to 2000 Th [*Junninen et al*., 2010; *Ehn et al*., 2010; *Schobesberger et al*., 2013]. During CLOUD5, the APi-TOF-MS usually operated in the negative mode, where sulfuric acid ions can be detected. The APi-TOF-MS is a key instrument in this study as it can differentiate clusters produced by pure binary processes, i.e., containing only sulfuric acid and water, from clusters also containing other molecular species. Even though not all trace gas contaminations could be detected directly in the gas phase, the APi-TOF-MS is sufficiently sensitive to determine if additional species are participating in the initial cluster formation, albeit with the limitation that it can only measure charged molecular clusters. The

Table 1. Estimated Cutoff Size Ranges of the Different Particle Counters Over the Course of the Campaign[a]

Particle Counter	Estimated Cutoff Size
PSMa	~1.3 ~ 1.6 nm
PSMb	~1.6 ~ 1.8 nm
DEGa	~2 nm
DEGb	~2.7 nm
UCPC	~3.2 nm

[a]The cutoff size corresponds to the mobility diameter at which 50% of the particles are detected, including sampling line losses. See Wimmer et al. [2015] for the details.

separation into "pure H_2SO_4/H_2O binary" or "contaminated" particle formation classes in this study is based on the molecular identification of the clustered species using the APi-TOF-MS. This procedure is further discussed in section 3.1.

2.2.3. Particle Number Concentration and Size Distribution Measurements

The particle formation rate was determined by a series of particle counters with cutoff sizes 3.2 nm. The counters enabled simultaneous constraints on formation and growth rates, which is essential to determine accurate values for both of the rates [Kürten et al., 2015]. They included one Ultrafine Condensation Particle Counter (UCPC, TSI 3776) with a cutoff size of 3.2 nm mobility diameter, two Particle Size Magnifiers (PSM, Airmodus A09), and two Diethylene-Glycol Condensation Particle Counters (DEG-CPCs). The PSMs and DEG-CPCs are state-of-the-art particle counters with adjustable particle size detection thresholds, using diethylene-glycol as a working fluid. The total inlet flow rate of the PSM is 2.5 L min^{-1}. It produces supersaturation by mixing the ambient-temperature aerosol flow with a flow of heated particle-free air from a DEG saturator; varying the saturator flow rate rapidly changes the supersaturation and determines the PSM cutoff size [Vanhanen et al., 2011]. The DEG-CPC works in a similar way as the PSM, except that instead of having a turbulent mixing in the DEG section, it employs a continuous laminar flow [Wimmer et al., 2013]. The temperature of the saturator flow is changed to alter the cutoff size. The two PSMs and the two DEG-CPCs were set to different fixed cutoff sizes, which have been determined in the laboratory using ammonium sulfate particles [Wimmer et al., 2013; Kangasluoma et al., 2013]. As the temperature of sampled air influences the cutoff size of the instrument [Wimmer et al., 2015], the instrumental settings were adjusted according to the sampling air temperatures (varying from 207 to 298 K) to keep an approximately fixed cutoff size through the entire campaign. An estimation of the mobility diameter cutoff sizes for each detector used during CLOUD5 is summarized in Table 1.

The particle size distribution in the ~7–120 nm range was measured with a scanning mobility particle spectrometer (SMPS). The SMPS consisted of a neutralizer (Krypton 85) and a short Differential Mobility Analyzer (short DMA) coupled to a CPC (TSI 3786). The neutralizer and the short DMA were in a temperature-controlled rack, matching the chamber temperature down to 248 K, and kept at this temperature for measurements at lower temperatures, whereas the CPC 3786 was at ambient temperature. The SMPS data were used to calculate the coagulation sink, making it possible to calculate loss-corrected particle formation rates in different size ranges.

To minimize the losses through the sampling probes and the consequent loss correction to apply to the data, core-sampling probes were used for all the particle instruments described above. The instruments drew samples via the core-sampling probe from the middle of the sample flow at an isokinetic rate, optimizing the sampling efficiency of the sampling probe, typically with a core flow of 2.5 L min^{-1} and a bypass flow of 5 L min^{-1} [Wimmer et al., 2015].

2.2.4. Gas Phase Measurements

Sulfuric acid was measured with a Chemical Ionization Mass Spectrometer (CIMS) from THS Instruments (THS Instruments LLC, USA). A detailed description of the instrument, its principle of operation, and its calibration can be found elsewhere [Eisele and Tanner, 1993; Berresheim et al., 2000; Petäjä et al., 2009; Kürten et al., 2011, 2012]. The CIMS measured sulfuric acid at a sampling frequency of 0.1 Hz. Its lower detection limit was estimated to be ~3×10^5 mol cm^{-3} for an integration time of 20 min. The CIMS setup, including the sampling line used at the CLOUD chamber, was calibrated with a calibration system that provided known and stable concentrations of sulfuric acid [Kürten et al., 2012]. The value reported here as sulfuric acid concentration corresponds only to the concentrations of monomer (potentially hydrated) sulfuric acid. The fraction of sulfuric acid in clusters with two or more sulfuric acid molecules is excluded.

SO_2 and O_3 were monitored using standard gas monitors (42i-TLE, Thermo Fisher Scientific Inc., and TEI 49C, Thermo Environmental Instruments, respectively). The water concentration was measured with two dew point

process in the stratosphere [*Merikanto et al.*, 2009]. QC-normalized CNT can be combined with global models to study the significance of neutral and ion-induced water-sulfuric acid particle formation in Earth's atmosphere. Another potentially interesting use of the QC-normalized CNT combined with global model is for the study of the atmospheres of other planets, particularly the Venusian atmosphere where water-sulfuric acid particle formation is also likely to be the dominant particle formation process [*Esposito et al.*, 2014].

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